Correlation of Infinite Dilution Diffusion Coefficients with Molar Volume

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Application of the Stokes-Einstein relationship between the diffusion coefficient D, the solution viscosity, implies an inverse relationship between D and the diffusing solute hydrodynamic radius, or alternatively the (1/3) power of the molar volume (n = 1/3). Real systems do follow a fractional power relation, but with values other than 1/3. For example, if one examines the dependence of the self-diffusion coefficient of water and of the tracer diffusion coefficients of a wide range of alcohols of varying molar volume, for which very precise data care available, n = 0.56. Comparisons are made for a number of families of solutes in aqueous solution with solutes in nonaqueous non-electrolyte solutions and molecular dynamics simulations of tracer diffusion and discussed in terms of solution structure.